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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Degreasing Process with Hydrogen Peroxide Especially for Metal Articles

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Notice: This application is as filed and may therefore contain an incomplete specification.

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ABSTRACT

The present invention relates to the use of a mixture consisting of an aqueous solution containing from 3 to 50 % by weight of hydrogen peroxide and of an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium, as degreasing composition especially for cleaning metal articles.

It relates, furthermore, to a degreasing process making use of this mixture.

Application: industrial degreasing in the engineering industry.

The present invention relates generally to the field of industrial degreasing and cleaning of manufactured articles and its subject-matter is chiefly the use of compositions based on hydrogen peroxide as degreasing agent especially for metal articles.

A mechanical article is subjected to various cleaning and degreasing treatments during its manufacture.

These treatments can be carried out either by means of aqueous solutions ("aqueous process"), or by means of solvents ("solvent process").

Petroleum solvents and chlorinated solvents are prominent among the solvents currently employed for making use of these latter treatments, the last-mentioned solvents being subdivided into two subgroups: chlorinated solvents and chlorofluorinated solvents.

Chlorinated solvents are employed chiefly for cleaning and degreasing of metals at various stages:

- degreasing between operations,
- final cleaning,
- degreasing before surface treatment,
- maintenance cleaning.

These solvents in fact offer many advantages in these applications.

In particular they have good degreasing properties, whatever the type of contamination to be cleaned off, and are compatible with all materials.

In addition, since their boiling point is relatively low, they can be employed in vapour phase with a relatively low expenditure of energy.

Finally, they can be employed hot practically without risk because they do not exhibit any flash point.

However, chlorinated solvents are toxic to man and detrimental to the environment, because they are, in particular, suspected of destroying the ozone layer.

For these reasons, chlorinated solvents are at present subject to a severe regulation intended to restrict, or even to prohibit, their use, in the

particular case of chlorofluorinated (CFC) solvents and of 1,1,1-trichloroethane (T111).

In these conditions the objective of the present invention is to solve the technical problem consisting of the provision of degreasing compositions capable of being employed as a replacement for the chlorinated solvents, with the same effectiveness as the latter but without exhibiting their disadvantages which were recalled above.

Another objective of the present invention is to solve the technical problem consisting in providing a process allowing these degreasing compositions to be used on an industrial scale.

It has been found, and this constitutes the basis of the present invention, that mixtures consisting of an aqueous solution containing from 3 to 50 % by weight of hydrogen peroxide and of an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium exhibit very good degreasing properties and can be advantageously employed for cleaning articles, especially metallic ones.

Some mixtures such as those employed within the scope of the present invention have already been described generically in document EP 0 351 772.

More precisely, this prior document describes in a general manner aqueous solutions of hydrogen peroxide containing a surface-active agent of any kind, the weight ratio of this surface-active agent to the hydrogen peroxide being between approximately 1:1 and 1:10 000.

It should be noted that, according to this prior document, the function of the surface-active agent is essentially:

- on the one hand, to stabilize the hydrogen peroxide solution against the catalytic activity of metal ions, and in particular of cupric ions, and

- on the other hand, to facilitate the rinsing of metal articles which are treated with a hydrogen peroxide solution.

However, document EP 351 772 does not comprise any indication liable to encourage a person skilled in the art to employ a surface-active agent in general and, a fortiori, a wetting surface-active agent in order to produce a degreasing composition based on hydrogen peroxide.

Thus, according to a first aspect, the invention aims to cover the use of a mixture consisting of an aqueous solution containing from 3 to 50 % and preferably from 10 % to 40 % by weight of hydrogen peroxide and of an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium, as degreasing composition especially for cleaning metal articles.

Many wetting surface-active agents can be employed within the scope of the present invention in order to improve the degreasing properties of aqueous solutions of hydrogen peroxide.

These surface-active agents may be anionic, nonionic, cationic or amphoteric.

Among the anionic agents capable of being employed there will be mentioned more particularly the organic mono-, di- and triesters of phosphoric acid, fatty acids and sulphonated esters, carboxylated ethoxylated fatty alcohols marketed especially under the name Akypo by the Chemy company, and alkylnaphthalenesulphonates.

Among the nonionic surface-active agents capable of being employed there will be mentioned more particularly:

- the following nonalkoxylated derivatives: alkylpolyglucosides, fatty acid alkanolamides and amine oxides;
- the following alkoxylated derivatives: alkoxylated alcohols and alkylphenols, copolymers of ethylene and propylene oxides,

ethoxylated fatty acids, ethoxylated sorbitan esters, ethoxylated glycerides, alkoxylated amines and amides and alkoxylated derivatives of perfluorinated and polyfluorinated alcohols.

Among the cationic surface-active agents capable of being employed there will be mentioned more particularly quaternary ammoniums and amine and imidazoline salts.

Finally, betaines will be mentioned more particularly among the amphoteric surface-active agents capable of being employed.

The best results have been obtained by employing nonionic wetting surface-active agents of hydrophilic nature and more particularly ethoxylated sorbitan esters.

The quantity of surface-active agents to be employed depends, of course, on the nature of the surfactant and on the general conditions of use of the degreasing treatment, but can be easily determined by a person skilled in the art.

In general, the weight ratio of the surface-active agent to hydrogen peroxide within the mixtures to be employed will be between 1:10 and 1:1000, preferably between 1:30 and 1:100.

The aqueous solution containing hydrogen peroxide may be prepared by diluting a concentrated solution of hydrogen peroxide in an aqueous medium.

Ethoxylated sorbitan esters employed in a weight ratio of approximately 1:100 with a 35% solution of hydrogen peroxide provide the currently preferred embodiment of the invention when working at 60°C.

When operating at 70°C the preferred solution includes, as active agent: from 10 to 15 % of the weight of hydrogen peroxide and from 0.3 to 0.5 % of ethoxylated sorbitan esters.

Among the ethoxylated sorbitan esters preferably employed within the scope of the present invention there will be mentioned in particular

ethoxylated sorbitan monolaurate and especially the product marketed under the name Montanox 20® by the Seppic company.

In a second aspect the subject-matter of the invention is an aqueous solution comprising, as active agent, 10 to 15 % by weight of hydrogen peroxide and 0.3 to 0.5 % by weight of ethoxylated sorbitan monolaurate.

In a third aspect, the subject-matter of the invention is an aqueous solution comprising, as active agent, 30 to 50 % by weight of hydrogen peroxide and 0.5 % to 1 % by weight of ethoxylated sorbitan monolaurate. Such a solution, ready for use, can be employed by being diluted to 1/2, or else without being diluted, as additive in order to readjust the hydrogen peroxide assay of the working solution during a degreasing operation.

One or more agent(s) stabilizing the hydrogen peroxide may be added to the mixture employed in accordance with the present invention, in order to increase the duration of use of the degreasing composition.

The compounds which will be mentioned in particular for this purpose are those which have the property of forming complexes with metals, like, for example, aminocarboxylic and aminophosphonic compounds, and stabilizers such as sodium stannate and sodium pyrophosphate, which are described in the literature.

According to a fourth aspect, the present application aims to cover a process for degreasing articles, especially metallic ones, characterized in that it consists:

- in immersing the said articles in a bath including a mixture consisting of an aqueous solution containing from 3 to 50 % by weight of hydrogen peroxide and an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium, at a temperature of between 15 and

100°C, preferably between 25 and 90°C, for a period of between 5 seconds and 60 minutes, preferably from 5 to 30 minutes, and,

- in rinsing the said articles thus treated.

The nature of the surface-active agent and the concentrations of hydrogen peroxide and of surface-active agent within the immersion bath are such as defined above.

The abovementioned immersion of the articles in the bath will advantageously be accompanied by a mechanical action intended to facilitate the contact between the articles and the bath.

This mechanical action may, for example, consist of the use of jets, of means for agitating the bath or articles, or else of the use of ultrasonics.

The temperature and duration conditions of the immersion stage depend especially on the concentrations of hydrogen peroxide and of surface-active agent.

In general, the duration of the immersion treatment will be proportionally shorter, the higher the bath temperature.

A person skilled in the art will have no difficulty in determining the appropriate temperature and duration conditions in each particular case.

DEMONSTRATION OF THE PROPERTIES OF THE MIXTURES EMPLOYED WITHIN THE SCOPE OF THE INVENTION

The degreasing properties of the mixtures of hydrogen peroxide and of surface-active agents were demonstrated in the following manner:

Stainless steel panels (10 cm × 10 cm) were contaminated in a controlled manner.

To this end a mixture of oil in hexane is sprayed onto a panel previously placed on a rotating tray.

The centrifugal force due to the rotation of the panel allows the oil mixture to spread on the surface of the latter and the quantity of oil sprayed

must be such that the panel is completely covered and that an excess of oil is thrown off at the side.

Both faces of each panel are thus prepared.

Weight measurements before and after contamination showed that the quantity of oil deposited on each face by this method was of the order of 2 mg, which corresponds to a concentration of 0.2 g/m2.

Thus contaminated, the panels are placed in beakers of sufficient size to enable the panel to lie flat in the beaker.

A support which is clean and inert towards hydrogen peroxide is placed between the bottom of the beaker and the panel, so as to permit free circulation of the solution to be tested, over the entire surface of the panel.

The hot tests were performed on a steam bath under an exhaust hood.

The bath is heated to the desired temperature until the thermal equilibria have been obtained, and the panel is then introduced into it.

The thermal inertia of the latter is sufficiently small not to result in a change in temperature when it is placed in position.

At the end of each test the treated panel is taken out of the bath and then rinsed with running water and finally dried in a vertical position.

The evaluation of the state of cleanliness of a surface is a tricky problem.

In fact, there is at present no simple, rigorous and absolute means for quantifying the cleanness of the surface of an article.

A method capable of being employed in order to evaluate the state of cleanness of a surface is the so-called "adhesive tape test".

This method consists in carefully applying a length of adhesive tape to the surface to be tested and in then removing it and bonding it onto a sheet of white paper.

It is assumed that the adhesive tape has entrained with it all the contamination at the spot where it has been in contact with the panel. In these conditions, when the adhesive tape is placed on the white sheet, the change in its colour can be assessed visually by referring to a preestablished scale.

It has not been possible, however, to apply this method in the case where the oil deposited onto the stainless panels is colourless, with the result that no change is seen in the colour of the adhesive tape.

The method which has been employed within the scope of the invention is an alternative form of the adhesive tape test, based on the finding of the fact that the colour of a clean panel is lighter than that of a contaminated panel.

Assuming that the adhesive tape removes all greasy contamination at the surface of the panel, a light trace should appear when the adhesive tape is removed after having been applied to a contaminated panel.

The evaluation of the degreasing action of the bath has therefore been performed using the evaluation of the trace thus produced.

To this end, a five-level evaluation scale has been established as a function of the trace left by the adhesive tape on the panel.

- Level 0: no effect, the panel has retained its original colour. It is, of course, very greasy to the touch.
- Level 1: perceptible effect with a slight change in colour, but much oil still remains detectable to the touch.
- Level 2: the oil coating is imperceptible to the touch, the trace of the adhesive tape is still visible, the edge of the trace being continuous.
- Level 3: the trace of the adhesive tape is invisible in places.

- Level 4: the trace of the adhesive tape is completely invisible.

RESULTS OF THE TESTS CARRIED OUT

Preliminary tests have shown the crucial role of the rinsing in the degreasing process in accordance with the invention.

In fact, on leaving the bath, the articles are covered with a liquid film containing hydrogen peroxide, surfactant and various materials originating from the contamination.

The latter, which are generally greasy and hydrophobic, tend to form micelles with the surfactant molecules.

On dyeing, the water and hydrogen peroxide evaporate and these micelles are redeposited at the surface of the article.

It is therefore particularly important to rinse the articles immersed in the degreasing bath to obtain the desired effect.

The results of the various tests which have demonstrated the detergent properties of the mixtures based on hydrogen peroxide and surfactants are reported in Table I.

The wetting surface-active agent employed within the scope of these tests is an ethoxylated sorbitan monolaurate (product Montanox 20®).

This surfactant is, of course, mentioned only by way of particular and preferred illustrative example but, as indicated above, a person skilled in the art will be capable of finding other compounds producing the required result, especially among the classes of surfactants referred to above.

Test No. 1 was carried out in relatively severe operating conditions, the hydrogen peroxide concentration being 35 % by weight, the temperature of the bath 70°C and the immersion period 30 minutes.

In these conditions the degreasing action is particularly remarkable.

In fact, after rinsing and drying, the abovementioned test shows that the panel is clean.

The following four tests (No. 2 to 5) were carried out to demonstrate the role of each of the constituents of the degreasing bath.

In these tests, the bath temperature is 70-75°C and the immersion period 15 minutes.

A bath consisting solely of distilled water is completely ineffective (test No. 3).

Hydrogen peroxide employed by itself produces only a relatively average result (test No. 4).

Similarly, the surface-active agent employed by itself yields a mediocre result (test No. 5).

On the other hand, the hydrogen peroxide-surfactant combination is found to be fully effective (test No. 2).

The following tests (No.6, 7 and 8) demonstrate the effect of the bath temperature on the degreasing action.

The results obtained show that the temperature of the bath is an important factor for obtaining the required result and that, in the case of a predetermined duration of treatment, there is a threshold value below which the treatment loses its effectiveness.

In the case of the surface-active agent employed in these tests, this threshold lies between 50 and 70°C in the case of an immersion period of 15 minutes.

The test at 60°C is found to be a relatively satisfactory compromise between the treatment period and the temperature of the bath for use in the mechanical industry.

The following tests (No. 9 to 14) demonstrate the influence of the period of immersion in the bath on the degreasing action.

The results obtained show that the immersion period is an important factor for obtaining the required result and that, for a predetermined bath temperature, there is a threshold value below which the treatment loses its effectiveness.

Tests No. 9 to 12, carried out between 80 and 87°C, show that the minimum period enabling an acceptable level of cleanness to be obtained is approximately 2.5 minutes.

Tests No. 13 and 14 show that a satisfactory result can be obtained at a bath temperature of 90°C and an immersion period of 2.5 minutes.

Thus, within the scope of the invention the immersion period can be reduced every time that this is found necessary, but, in this case, the bath temperature must be increased to arrive at the required result.

The following tests (No. 15 to 17) have shown that it is still possible to reduce the immersion period and the bath temperature simultaneously when the immersion treatment is assisted by a treatment such as the use of ultrasonics.

Thus, good results can still be obtained in these conditions with an immersion period of the order of 1 minute and a bath temperature of the order of 70°C.

The following test (No. 18) shows that the concentration of surface-active agent is an important factor for obtaining the required result and that for a predetermined immersion period and bath temperature, there is a threshold value below which the treatment loses its effectiveness.

In the case where the surface-active agent is an ethoxylated sorbitan monolaurate, an optimum concentration of surfactant is 3.5 g/l in the treatment conditions that can be employed on an industrial scale.

Tests No. 19 and 20 show that the concentration of hydrogen peroxide which is necessary to obtain the required result depends on the bath temperature.

Test 20 in particular shows that it is possible to employ 15% solutions of H_2O_2 if the bath temperature is increased to 70°C and that, after an immersion for approximately 5 minutes, the result obtained is rated 3+.

To evaluate the stability of the solution, the hydrogen peroxide concentration and the pH have been measured at regular intervals.

The results obtained show that the pH of the bath remains appreciably constant before and after cleaning, at a value of approximately 2.5.

On the other hand, the hydrogen peroxide assay increases slightly during the treatment, probably because of the fact that evaporation tends to concentrate the peroxide solution.

However, this phenomenon is relatively negligible.

The process in accordance with the present invention offers many advantages.

Most importantly, it is appropriate to note that this process can be easily implemented on existing plants, practically without contamination, insofar as the chemical agents that can be employed are generally biodegradable.

TABLE I

TEST	H2O2 Concentration (% by weight)	Surfactant concentration (9/1)	Temperature (°C)	Time (min)	Mark
1	35	3.5	70	30	4
2	35	3.5	75	15	4
3	0	0	75	15	0
4	35	0	75	15	2
5	0	3.5	75	15	1
6	35	3.5	50	15	2+
7	35	3.5	90	15	[illegible]
8	35	3.5	60	15	3+
9	35	3.5	80	2	1+
10	35	3.5	85	2.5	3+
11	35	3.5	85	2	1
12	35	3.5	87	2.5	3+
13	35	3.5	90	2	3
14	35	3.5	90	2.25	4-
15	35	3.5	81	1	4
16	35	3.5	76	1	3+
17	35	3.5	70	1	3+
18	35	1.5	60	15	2
19	15	3.5	60	15	2
20	15	3.5	70	5	3+

2181416

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. Use of a mixture consisting of an aqueous solution containing from 3 to 50 % and preferably from 10 to 40 % by weight of hydrogen peroxide and of an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium, as degreasing composition especially for cleaning metal articles.

2. Use according to Claim 1, characterized in that the abovementioned wetting surface-active agent(s) is are) chosen from the group including the organic mono-, di- and triesters of phosphoric acid, fatty acids and sulphonated esters, carboxylated ethoxylated fatty alcohols and alkylnaphthalenesulphonates, alkylpolyglucosides, fatty acid alkanolamides and amine oxides, alkoxylated alcohols and alkylphenols, copolymers of ethylene and propylene oxides, ethoxylated fatty acids, ethoxylated sorbitan esters, ethoxylated glycerides, alkoxylated amines and amides, alkoxylated derivatives of perfluorinated and polyfluorinated alcohols, quaternary ammoniums, amine and imidazoline salts and betaines.

3. Use according to Claim 1 or 2, characterized in that the abovementioned wetting surface-active agent(s) is (are) chosen from nonionic surfactants of hydrophilic nature and in particular from ethoxylated sorbitan esters.

4. Use according to one of Claims 1 to 3, characterized in that the weight ratio of the surface-active agent(s) to the hydrogen peroxide within the said mixture is between 1:10 and 1:1000, preferably between 1:30 and 1:100.

5. Use according to one of Claims 1 to 4, characterized in that the abovementioned aqueous solution includes 35 % by weight of hydrogen peroxide.

6. Use according to one of Claims 1 to 4, characterized in that the abovementioned aqueous solution includes from 10 to 15 % by weight of hydrogen

peroxide and 0.3 to 0.5 % of ethoxylated sorbitan esters.

7. Aqueous solution comprising, as active agent, 10 to 15 % by weight of hydrogen peroxide and 0.3 to 0.5 % by weight of ethoxylated sorbitan monolaurate.

8. Aqueous solution comprising, as active agent, 30 to 50 % by weight of hydrogen peroxide and 0.5 % to 1 % by weight of ethoxylated sorbitan monolaurate.

9. Process for degreasing articles, especially metallic ones, characterized in that it consists:

- in immersing the said articles in a bath including a mixture consisting of an aqueous solution containing from 3 to 50 % by weight of hydrogen peroxide and of an effective quantity of at least one wetting surface-active agent which is stable in an oxidizing medium, at a temperature of between 15 and 100°C, preferably between 25 and 90°C, for a period of between 5 seconds and 60 minutes, preferably from 5 to 30 minutes,
- in rinsing the said articles thus treated.

10. Process according to Claim 9, characterized in that the abovementioned immersion of the articles in the bath is accompanied by a mechanical action intended to facilitate the contact between the articles and the bath, like, in particular, the use of ultrasonics.

11. Process according to one of Claims 9 and 10, characterized in that the bath is a solution such as defined in Claim 5 at a temperature of approximately 60°C.

12. Process according to one of Claims 9 and 10, characterized in that the bath is a solution such as defined in Claim 7 and that the operating temperature is approximately 70°C.

13. Process according to one of Claims 9 and 10, characterized in that the bath is a solution such as defined in Claim 8, diluted by a half and that the operating temperature is approximately 70°C.